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237

Synthesis and Characterization of Poly(Arylene Ether Benzimidazole) Oligomers

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Abstract

Several poly(arylene ether benzimidazole) oligomers were prepared by the nucleophilic aromatic substitution reaction of a bisphenol benzimidazole and various alkyl-substituted aromatic bisphenols with an activated aromatic dihalide in *N,N*-dimethylacetamide. Moderate to high molecular weight terpolymers were obtained in all cases, as shown by their inherent viscosities, which ranged from 0.50 to 0.87 dL g⁻¹. Glass transition temperatures (*T_g*s) of polymer powders ranged from 267-280°C. Air-dried unoriented thin film *T_g*s were markedly lower than those of the powders, whereas *T_g*s of films dried in a nitrogen atmosphere were identical to those of the corresponding powders. In addition, air-dried films were dark amber and brittle, whereas nitrogen-dried films were yellow and creasable. Nitrogen-dried films showed slightly higher thin-film tensile properties than the air-dried films, as well.

Introduction

Polybenzimidazoles (PBIs) are heterocyclic polymers which exhibit high chemical, physical, and mechanical properties. They are generally prepared via the two-phase melt condensation reaction of a tetrafunctional bis(*o*-diamine) with a dicarboxylic acid, or derivatives thereof, at temperatures around 260°C¹. This reaction can also be carried out in polyphosphoric acid². The polymers are well known for their thermal stability, which is derived from the high resonance energy of the aromatic and heterocyclic groups incorporated into the chain¹, as well as from intermolecular hydrogen bonding effects. Also characteristic of PBIs are their excellent solvent resistance, resistance to acid/base hydrolysis, and hydrophilicity. However, despite their advantages, PBIs are notoriously difficult and expensive to process, requiring extremely high molding temperatures and pressures. As a result, these materials are not extensively used. Some PBI applications include: nose cones for airborne projectiles, heat-resistant *o*-rings and gaskets, and varnishes³. PBI is commercially sold under the name of Celazole^{®3}.

Poly(arylene ether)s (PAEs) are a class of engineering thermoplastics which show great potential for use in high-performance applications. They are generally synthesized by the nucleophilic aromatic substitution reaction of an activated aromatic dihalide and the alkali metal salt of an aromatic bisphenol in polar, aprotic solvents⁴. Other methods of PAE preparation include electrophilic Friedel-Crafts processes⁵, macrocyclic ring cleavage⁶, and oxidative coupling reactions⁷. Since PAEs are thermoplastic materials, they are much easier to process than the thermoset-like polybenzimidazoles, and their low flammability/low gas emission during thermal stresses make them well-suited for high-performance aerospace applications. These materials generally show excellent solvent resistance, with the exception of their characteristic swelling in chlorinated solvents. This susceptibility to chlorinated substances, which are commonly used in the aerospace industry, have prevented the widespread use of PAEs in this area. However, PAEs are quite common commercially, with applications that include artificial heart casings, pin grid array sockets, molded circuit boards, fiber optic connectors, and cable insulation⁸.

By incorporating heterocyclic units into PAEs, it is possible to obtain a combination of the high chemical and thermal resistance of heterocyclic polymers with the ease of processability of PAEs. Two routes have been established to these materials. The first route involves the nucleophilic aromatic displacement reaction of a heterocyclic-containing, activated aromatic dihalide with the alkali metal salt of an aromatic bisphenol in polar, aprotic solvents^{9,10}. The

second method involves the reaction of the alkali metal salt of a heterocyclic-containing aromatic bisphenol with an activated aromatic dihalide under similar conditions^{11,12}. Examples of heterocyclic units which have previously been incorporated into PAEs include: quinoxalines⁹, imidazoles¹², 1,3,4-oxadiazoles¹³, and 1,2,4-triazoles¹³.

The objective of this study is to prepare high-temperature, chemically resistant, and potentially photopatternable poly(arylene ether benzimidazole)s for potential aerospace and microelectronics applications.

Approach

Synthesize controlled molecular weight poly(arylene ether benzimidazole) (PAEBI) random terpolymers via the nucleophilic aromatic displacement of 5,5'-bis[2-(4-hydroxyphenyl) benzimidazole] and various alkyl-substituted aromatic bisphenols with 4,4'-difluorobenzophenone, using 4-fluorobenzophenone as the endcapping agent.

Experimental

Starting materials

4,4'-Difluorobenzophenone (m.p. 103-106°C, Lancaster Synthesis) was recrystallized from absolute ethanol. 4-Fluorobenzophenone (m.p. 46-48°C, Lancaster Synthesis) and 5,5'-bis[2-(4-hydroxyphenyl) benzimidazole] (m.p. 389°C, Technically) were used as received. Tetramethyl bisphenol A (TM-BPA, m.p. 163-166°C), dimethyl bisphenol A (DM-BPA, m.p. 137-139°C), bisphenol E (BPE, m.p. 122-126°C), tetramethyl bisphenol F (TM-BPF, m.p. 174-175°C), bisxylenol P (m.p. 159-161°C), hexamethyl biphenol (HM-BPL, m.p. 225-228°C), and tetramethyl biphenol (TM-BPL, m.p. 219-224°C) were obtained from Ken Seika Corp., and were used as received. Other reagents were obtained from commercial sources and used as received.

Polymer Synthesis

Poly(arylene ether benzimidazole)s (PAEBIs) were prepared by reacting a 6% excess of a 3:1 molar ratio of 5,5'-bis[2-(4-hydroxyphenyl) benzimidazole] (75 mol %) and alkyl-substituted bisphenol (25 mol %) with 4,4'-difluorobenzophenone (94 mol %) in the presence of pulverized potassium carbonate in anhydrous N,N-dimethylacetamide (DMAc) at 15% solids (wt/wt). 4-Fluorobenzophenone (12 mol %) was used as the endcapper. The water generated during the alkali metal formation of the bisphenate was removed as an azeotrope with toluene. The reaction mixture was stirred at 155-160°C under a nitrogen atmosphere for 12-16 hours to afford dark brown, viscous solutions. The reaction mixtures were precipitated into a water/acetic acid mixture (~10/1), washed successively in hot water and methanol to remove trapped salts, and dried at ~90°C for ~12 hours to afford the off-white polymers in nearly quantitative yields

Films

DMAc solutions (10-25% solids wt/vol) of the polymers were centrifuged for approximately 1 hour, and the decantate was doctored onto clean, dry plate glass. The films were dried to a tack-free form in a low-humidity chamber, and subsequently dried at 100, 200, and

The molecular weights of the polymers were controlled by offsetting the stoichiometry in favor of the bisphenols and endcapping with 4-fluorobenzophenone. The alkyl-substituted aromatic bisphenols (Ar) used in the preparation of the terpolymers are shown in Figure 1.

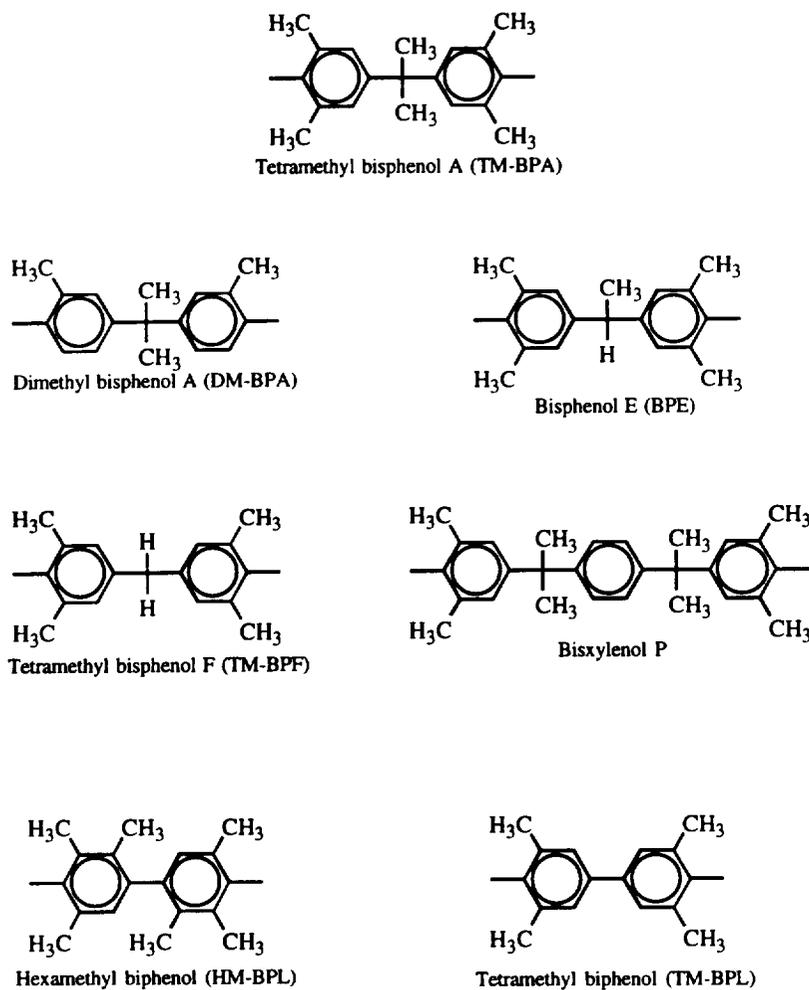


Figure 1

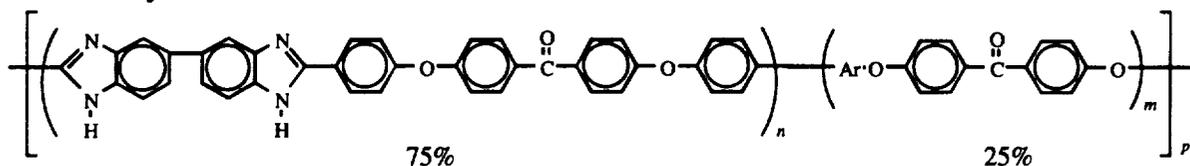
Generally, polymerizations required the full 16-24 hours to reach completion, as the reaction mixtures did not become significantly viscous before this time. Nearly quantitative yields were obtained for all the polymers, except for the TM-BPF-containing terpolymer, which was obtained in 63% yield. The low yield of this material was due to the formation of insoluble material (gel) in the extremely viscous reaction mixture, presumably due to hot spots in the reaction medium which form as a result of inefficient heat transfer in viscous solutions¹⁴. Employing a higher degree of stoichiometric offset or a lower solids content of the reaction mixture would probably solve this problem. Subsequent preparation of the TM-BPF-containing PAEBI at an 8% stoichiometric offset afforded the same results with an overall yield of 46%. Polymer characterization is presented in Table 1.

Glass transition temperatures ranged from 261-280°C, and inherent viscosities ranged from 0.47 to 0.87 dL g⁻¹, which indicates that moderate to high-molecular weights were obtained. These values compare well with results obtained from similar PAEBIs previously prepared¹⁴.

Trends in PAEBI T_gs can be based on three characteristics of the alkyl-substituted aromatic bisphenols: (1) the presence and substitution of the linkage unit joining the two phenyl rings, (2) the methyl substitution on the phenyl rings of DM-BPA and TM-BPA, and (3) the methyl substitution on the phenyl rings of the biphenol structures, TM-BPL and HM-BPL. In the first case, the observed T_g trend with respect to the linkage unit is nil > CH₂ > CH-CH₃ > C(CH₃)₂ > 1,4-disopropylidylphenylene (TM-BPL > TM-BPF > BPE > TM-BPA > Bisxylenol P). Since the inherent viscosities of the materials being compared are dissimilar, and consequently the molecular weights of the polymers, the trends observed here could be due in part to molecular weight effects.

Regarding the second category, the tetramethyl substitution on TM-BPA as opposed to the dimethyl substitution on DM-BPA may affect the T_g in terms of steric effects between polymer chains. The more sterically hindered TM-BPA may show a higher T_g due to a lesser degree of chain mobility versus DM-BPA. Thirdly, the hexamethyl substituted HM-BPL may give a higher T_g than the less hindered TM-BPL for similar steric reasons. However, for both cases, no T_g was detected for either the TM-BPA or HM-BPL-containing PAEBIs by DSC.

Table 1 Polymer Characterization



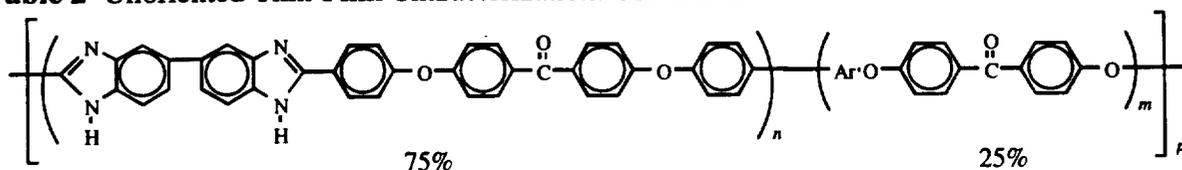
Ar	η_{inh} (dL g ⁻¹) ^a	T _g (°C) ^b
TM-BPL	0.87	280
TM-BPF ^c	0.82	271
BPE	0.47	267
DM-BPA	0.50	261
HM-BPL	0.73	Not Detectable by DSC
TM-BPA	0.64	Not Detectable by DSC
Bisxylenol P	0.61	TBD ^d

^a Inherent viscosity measured in DMAc on 0.5% (wt/vol) solutions at 25°C

^b Glass transition temperature determined by DSC at heating rate of 20°C min⁻¹

^c Polymerization carried out at 8% stoichiometric offset

^d TBD = to be determined

Table 2 Unoriented Thin-Film Characterization: Air-Dried

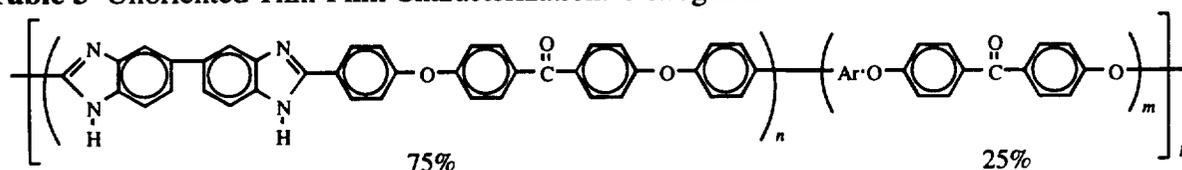
Ar	T_g ($^{\circ}\text{C}$) ^a	Color, texture ^b
TM-BPL	234	Amber, not creasable
TM-BPF ^c	239	Amber, not creasable
BPE	230	Amber, not creasable
DM-BPA	TBD ^d	Amber, not creasable
HM-BPL	Not Detectable by DSC	Amber, not creasable
TM-BPA	TBD	TBD
Bisxylenol P	TBD	TBD

^a Glass transition temperature determined by DSC at heating rate of $20^{\circ}\text{C min}^{-1}$

^b All films dried at 100, 200, and 300°C for 1h at each temperature

^c Polymerization carried out at 8% stoichiometric offset

^d TBD = to be determined

Table 3 Unoriented Thin-Film Characterization: Nitrogen-Dried

Ar	T_g ($^{\circ}\text{C}$) ^a	Color, texture ^b
TM-BPL	281	Light yellow, creasable
TM-BPF ^c	277	Light yellow, creasable
BPE	270	Light yellow, creasable
DM-BPA	271	Light yellow, creasable
HM-BPL	280	Light yellow, creasable
TM-BPA	TBD ^d	TBD
Bisxylenol P	TBD	TBD

^a Glass transition temperature determined by DSC at heating rate of $20^{\circ}\text{C min}^{-1}$

^b All films dried at 100, 200, and 300°C for 1h at each temperature

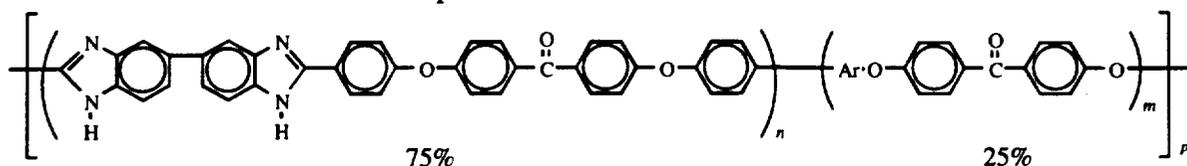
^c Polymerization carried out at 8% stoichiometric offset

^d TBD = to be determined

Unoriented thin-film properties are presented in Tables 2-5. Polymer films dried in air afforded amber, brittle films. However, drying films cast from the same polymer solutions in a nitrogen atmosphere, under the same temperature profile, yielded light yellow, creasable films. In addition, the T_g s of the air-dried films were considerably lower (~ 31 - 47°C) than those of the respective as-isolated powders, whereas the nitrogen-dried film T_g s correlated well with the as-isolated powder T_g s. This decrease in the thermal stability of the air-dried films was surprising,

and may be due to some oxidative degradation; since the films dried in an inert atmosphere showed no T_g decrease.

Table 4 Unoriented Thin-Film Properties^a: Air-Dried



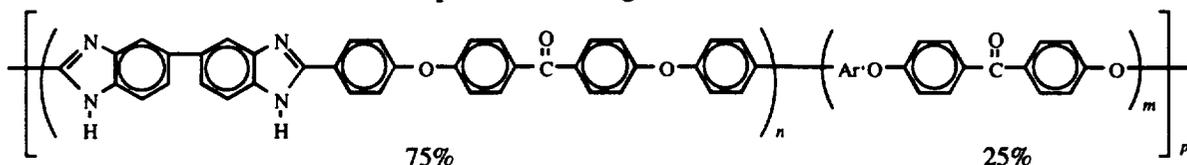
Ar	Tensile Strength (ksi)	Tensile Modulus (ksi)	Elongation at Break (%)
TM-BPL	17.7	484	7
TM-BPF ^b	TBD ^c	TBD	TBD
BPE	14.5	467	4
DM-BPA	TBD	TBD	TBD
HM-BPL	TBD	TBD	TBD
TM-BPA	TBD	TBD	TBD
Bisxylenol P	TBD	TBD	TBD

^a Films tested according to ASTM D882 at 23°C using four specimens per test

^b Polymerization carried out at 8% stoichiometric offset

^c TBD = to be determined

Table 5 Unoriented Thin-Film Properties^a: Nitrogen-Dried



Ar	Tensile Strength (ksi)	Tensile Modulus (ksi)	Elongation at Break (%)
TM-BPL	18.9	494	10
TM-BPF ^b	TBD ^c	TBD	TBD
BPE	17.7	475	10
DM-BPA	TBD	TBD	TBD
HM-BPL	TBD	TBD	TBD
TM-BPA	TBD	TBD	TBD
Bisxylenol P	TBD	TBD	TBD

^a Films tested according to ASTM D882 at 23°C using four specimens per test

^b Polymerization carried out at 8% stoichiometric offset

^c TBD = to be determined

This degradation could be due to the presence of abstractable primary benzylic hydrogens, which could be induced to form free radicals upon heating in the presence of oxygen. If this is the case, events such as α -chain scission adjacent to carbonyl groups or radical recombination to form lower molecular weight polymer chains could occur. Further investigation will be required before a more definitive conclusion can be drawn.

Unoriented thin-film properties of the nitrogen-dried films were slightly greater than those for films dried in air under similar conditions. As previously mentioned, films dried in air were darker in color and not creasable, whereas nitrogen-dried films were light yellow and creasable.

Conclusions

Moderate to high molecular weight poly(arylene ether benzimidazole) terpolymers were synthesized via the nucleophilic aromatic displacement reaction of 5,5'-bis[2-(4-hydroxyphenyl)benzimidazole] and various alkyl-substituted aromatic bisphenols with 4,4'-difluorobenzophenone. Air-dried polymer films exhibited more color, lower T_g s, and slightly lower unoriented thin-film tensile properties as compared to nitrogen-dried films. Characterization studies are still in progress, the results of which will be reported in future work.

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